# Extraction Rate of Nickel with 5-Dodecylsalicylaldoxime in a Vibro-Mixer

Takashi SANA[b], Koichiro SHIOMORI[a*] and Yoshinobu KAWANO[a]

[a]Department of Applied Chemistry, University of Miyazaki, Miyazaki 889-2192, Japan

[b]Yoshitama Surface Finishing Co., LTD, Nobeoka 882-0024, Japan

*Corresponding author: Tel & Fax +81-985-58-7309.

*E-mail address*: shiomori@cc.miyazaki-u.ac.jp

**Abstract**

In order to construct a recovery process of nickel from the wastewater of electroless nickel-plating, the extraction of nickel in aqueous ammonium sulfate solution with 5-dodecylsalicylaldoxime in kerosene was carried out using a vibro-mixer type continuous extractor, which has multiple vibration disks in a cylindrical tube. The effects of the initial concentrations of extractant, nickel, and proton, and the mean residence time of both solutions in the extractor on the extraction rate of nickel, were measured.

The experimental results correlated to the complete mixing flow of both fluids in the extractor were analyzed based on the interfacial reaction rate. The calculated results for each frequency number of the vibration plates was well explained by the experimental results. The average extraction rate in the vibro-mixer type extractor was interpreted based on a similar interfacial reaction equation derived in a Lewis type transfer cell. The average extraction rate constants obtained in the vibro-mixer type extractor were $10^2$- to $10^3$-fold larger than that in the Lewis type transfer cell. The mixing using the vibro-mixer type extractor generates and regenerates small droplets at high speed, causing enhancement of the interfacial area and the surface renewal rate.

## 1. Introduction

Recently, studies on the treatment of electroless nickel-plating wastewater using solvent extraction have appeared. Brooks [1] applied the solvent extraction method to wastewater, and found that the recovery yield of nickel extracted from the wastewater was 95%, which yield was not sufficiently high to offset the cost. Niinae et al. [2] reported on the applicability of some extractants to recover nickel from electroless nickel plating wastewater, though no effective extractant for nickel from the acidic spent bath could be found. Tanaka et al. [3] reported on the extraction equilibrium of nickel, and found that the recovery yield of nickel extracted from the wastewater is over 99%. Investigation of the extraction rate has never been carried out. We investigated the recovery process of valuable compounds from electroless nickel plating wastewater using solvent extraction. The equilibrium and the interfacial reaction rate of nickel with 5-dodecylsalicylaldoxime [4,5], the equilibria of some organic acids [6], and hypophosphorous, phosphorous, and phosphoric acids [7] with tri-*n*-octylamine have been reported. These findings represent basic knowledge of the separation and recovery process of valuable substances from wastewater of electroless nickel plating. In order to design a new wastewater treatment process of electroless nickel-plating, it is important to develop an efficient extraction process and to clarify the extraction rate in the process.

Solvent extraction is usually carried out in heterogeneous systems, which consist of an organic solvent containing extractants and an aqueous solution containing target substances. It is important to increase the contact surface area to achieve high extraction efficiency. Forced mixing type extractors, such as centrifugal or mixer/settler extractors, have been generally used as high efficiency contactors. However, there are some difficulties in keeping operations stable at high efficiency over a long period of time in such an apparatus. In our previous papers, we have reported that a vibro-mixer

type reactor, which has multiple vibration disks in a cylindrical tube, is suitable for the reaction of a heterogeneous phase system such as biological hydrolysis of lipids [8] and solvent extraction [9]. The vibro-mixer type reactor is able to produce small droplets continuously and steadily; to facilitate the average reaction rate in the reactor due to high surface renewal by the vibration of the disks; and to obtain rapid separation of both phases [8, 9].

In this study, the extraction rate of nickel in the aqueous ammonium sulfate solution with 5-dodecylsalicylaldoxime (hereafter called LIX860-IC or HR) in kerosene was investigated using the vibro-mixer type extractor. The effect of the concentrations of nickel and proton in the aqueous solution, the concentration of the extractant in the organic solution, and the average residence time of both fluids in the extractor on the extraction rate were measured. The experimental results correlated to the complete mixing flow into the vibro-mixer type extractor were analyzed based on the interfacial reaction rate, and the average extraction rate constants of each frequency were clarified. The effect on the reaction rate using the vibro-mixer type extractor was also discussed.

## 2. Experimental

### 2.1 Reagents

LIX860-IC (87.4 %, Cognis Japan Co.) was used as an extractant without further purification. Kerosene, $NiSO_4$, $NH_4OH$, and $(NH_4)_2SO_4$ were guaranteed reagents from Wako Pure Chemicals Co. and used without further purification.

An organic solution was prepared by dissolving LIX860-IC into kerosene. An aqueous phase was prepared by dissolving nickel sulfate in 0.5 mol/dm$^3$ aqueous ammonium sulfate solution. In order to adjust the pH values in the aqueous phase, ammonia aqueous solution was added to the aqueous solution. The proton concentration

in the aqueous solution was measured by pH meter (Horiba Co. F-12 pH meter). The nickel concentration in the aqueous solution was determined by atomic absorption spectrophotometry (Hitachi Co. Ltd., Z-8000 type). The initial extractant concentration in the organic solution was calculated from the weight of the extractant added in kerosene.

## 2.2    Measurement of the extraction rate

The vibro-mixer type extractor [8,9] (Reica Co.) used for the extraction of nickel in aqueous ammonium solution with LIX860-IC in kerosene is shown in **Fig. 1.** The extractor is a cylindrical glass tube with a $2.27 \times 10^{-2}$ dm$^3$ net volume, 18 mm i.d, and 9.6 cm height. The extractor is equipped with a shaft with multiple disk plates that is connected to the crankshaft of a motor. The vertical amplitude of the vibration plates is about 4.6 mm. The experimental apparatus is shown in **Fig. 2**. The organic and the aqueous solutions were stored in a water bath at 303 K. The organic and aqueous solutions were introduced into the inlets at the bottom of the extractor at the same flow rate, then started to vibrate the vibration plates at the constant frequency number. Both solutions flowed to the upper part from the lower part of the extractor, and the two solutions were sufficiently mixed by the vibration of the plates. The mixing solution flowed out through an outlet in the upper part of the extractor. After that the mixing of the both solutions in the extractor was attained to the steady state, the mixed solution emerging from the outlet was collected in a beaker as the sample. The sample was allowed to settle and separate in the beaker. The concentrations of nickel and proton in the aqueous solution were measured. The concentration of nickel in the organic solution was calculated by the mass balance from nickel concentration in the aqueous solution at the inlet and outlet of the extractor.

# 3. Results and Discussion

## 3.1 Extraction of nickel in the vibro-mixer type extractor

The extraction of nickel with LIX860-IC in the vibro-mixer type extractor was carried out under various conditions. When the average residence time of the fluid in the extractor, $\tau$, was 20 sec, the nickel concentration extracted in the organic solution, $C_{Ni,org}$, was plotted against the frequency of the vibration plates for various initial concentrations of nickel in the aqueous phase, $C_{Ni,aq,0}$, as shown in **Fig.3**. $C_{Ni,org}$ increased with increasing the frequency of the vibration plates in the extractor at a frequency lower than 500 strokes per minute (hereafter called spm), and increased with increasing $C_{Ni,aq,0}$.

When $\tau$ was 30 sec, $C_{Ni,org}$ was plotted against the frequency of the vibration plates for various $C_{Ni,aq,0}$, as shown in **Fig. 4**. $C_{Ni,org}$ increased with increasing the frequency of the vibration plates at a frequency lower than 500 spm, and increased with increasing $C_{Ni,aq,0}$.

$C_{Ni,org}$ was plotted against the frequency of the vibration plates for various initial concentrations of the extractant in the organic phase, $C_{HR,org,0}$, as shown in **Fig. 5**. $C_{Ni,org}$ increased with increasing the frequency of the vibration plates at a frequency lower than 500 spm, and increased with increasing $C_{HR,org,0}$.

$C_{Ni,org}$ was plotted against the frequency of the vibration palates for various pH values as shown in **Fig. 6**. $C_{Ni,org}$ increased with increasing frequency of the vibration plates at a frequency lower than 500 spm, and increased with decreasing pH.

$C_{Ni,org}$ was plotted against the frequency of the vibration plates for various mean residence times of both solutions in the extractor, $\tau$, as shown in **Fig. 7**. $C_{Ni,org}$ increased with increasing frequency of the vibration plates of the extractor at a frequency lower than 500 spm, and increased with increasing $\tau$. The experimental

results at 800 spm in Figs. 3-7 showed large scatter compared with those below 500 spm, and were the reason for the scattering is unknown.

### 3.2   Analysis of the extraction rate of nickel in the vibro-mixer type extractor

The extraction equilibrium of nickel in the ammonium sulfate solution with LIX860-IC in kerosene has been reported in a previous paper [4]. The experimental results were analyzed by graph fitting analysis [10], and were interpreted by the reaction model to form a (1:2) complex type of nickel and LIX860-IC, which is the complex between one molecule of nickel and two molecules of LIX-860-IC. The equilibrium constant was shown by the following equation [4]:

$$\text{Ni}^{2+} + 2\ \text{HR} \rightleftarrows \text{NiR}_2 + 2\text{H}^+ \qquad ; K \qquad (1)$$

$$K = C_{\text{NiR2,org}} C^2_{\text{H}^+,\text{aq}} / (C_{\text{Ni,aq}} C^2_{\text{HR,org}}) = 7.2 \times 10^{-6} \quad [\text{-}]. \qquad (2)$$

Further, the interfacial reaction was assumed to proceed by the following consecutive four steps:

$$\text{HR}_{\text{org}} + \theta_v \rightleftarrows \theta_{\text{HR}} \qquad\qquad ; K_{\text{HR}} \quad :\text{Step 1} \qquad (3)$$

$$\text{Ni}^{2+}_{\text{aq}} + \theta_{\text{HR}} \rightleftarrows \theta_{\text{NiR+}} + \text{H}^+ \qquad ; K_2 \quad :\text{Step 2} \qquad (4)$$

$$\theta_{\text{NiR+}} + \text{HR}_{\text{org}} \rightleftarrows \theta_{\text{NiR2}} + \text{H}^+_{\text{aq}} \qquad ; K_3 \quad :\text{Step 3} \qquad (5)$$

$$\theta_{\text{NiR2}} \rightleftarrows \text{NiR}_{2\text{org}} + \theta_v \qquad\qquad ; 1/K_{\text{NiR2}} :\text{Step 4} \quad . \qquad (6)$$

Step 1 is the adsorption of LIX860-IC into the interface from the organic solution. Step 2 is the reaction between nickel ion in the aqueous solution and LIX860-IC adsorbed on the interface to form a (1:1) complex ($\text{NiR}^+$) on the interface. LIX860-IC in the organic solution further reacts with the (1:1) complex to form the (1:2) complex ($\text{NiR}_2$) on the interface (Step 3). Step 4 is the desorption step of the (1:2) complex from the interface into the organic solution. The equilibrium of the interfacial adsorption of LIX860-IC and the (1:2) complex ($\text{NiR}_2$) to the interface of the aqueous and the organic solutions has been clarified from the interfacial tension of the aqueous and the organic solutions

under various conditions, which were analyzed based on Gibb's adsorption isotherm [5].

Further, the extraction rate of nickel in the ammonium sulfate solution with LIX860-IC in kerosene has been measured using a Lewis-type transfer cell [5]. The extraction rate of nickel in Lewis-type transfer cell was explained by the interfacial reaction model in which Step 3 in the above reaction processes was the rate-determining step. The interfacial reaction rate of the nickel extraction with LIX860-IC was determined as the following equation [5]:

$$r_{Ni} = k_0 \frac{K_{HR} K_2 C_{HR,org}^2 C_{Ni,aq}}{C_{H+,aq} + K_{HR} C_{HR,org} C_{H+,aq} + K_{HR} K_2 C_{Ni,aq} C_{HR,org}} \quad . \tag{7}$$

The values of the rate constant were determined by analysis of the extraction rate based on the rate equation using the results of the extraction equilibrium constant and the interfacial adsorption equilibrium of LIX860-IC and the (1:2) complex ($NiR_2$). In the Lewis-type transfer cell, the value of $k_0$ was the interfacial reaction constant in which the reaction proceeded only at the static interface of the aqueous and the organic solutions under moderate stirring.

In the vibro-mixer type extractor, the fractional extraction of nickel, $E$, is expressed by following equation:

$$E = (C_{Ni,aq,0} - C_{Ni,aq}) / C_{Ni,aq,0} \quad . \tag{8}$$

Assuming the complete mixing of the both solutions in the extractor [8,9], the average extraction rate, $r'_{Ni}$, per unit volume in the extractor is expressed as follows:

$$r'_{Ni} = (C_{Ni,aq,0} - C_{Ni,aq}) / \tau \quad . \tag{9}$$

where as $\tau$ is average residence time of the fluid in the extractor.

Considering Eqs. (8) and (9), the average extraction rate is transformed as follows:

$$r'_{Ni} = C_{Ni,aq,0} E / \tau \quad . \tag{10}$$

The average extraction rate of nickel in the extractor was assumed to be controlled by the interfacial reaction rate between nickel and LIX860-IC, and the concentration

dependencies of the species involved with the reaction would be similar in both types of reactor. The reaction on the interface in the vibro-mixer type extractor and in the Lewis-type transfer cell would proceed in a same manner. In the vibro-mixer type extractor, the droplets of the organic solution are dispersed in the aqueous phase. Furthermore, a new interface is always generated by new droplet formation by the vibration of the plates in the extractor. In the vibro-mixer type extractor, the interface of both solutions was always renewed, and a very large surface area was formed by small droplet formation.

The average reaction rate per unit volume in the vibro-mixer type extractor, Eq. (10), and the reaction rate per unit interfacial area in the Lewis-type transfer cell, Eq. (7), were discussed. The following equation is derived from Eqs. (10) and (7):

$$\frac{C_{\text{Ni,aq,0}}E}{\tau} = k_{\text{T}} \frac{K_{\text{HR}}K_2 C^2_{\text{HR,org}} C_{\text{Ni,aq}}}{C_{\text{H+,aq}} + K_{\text{HR}}C_{\text{HR,org}}C_{\text{H+,aq}} + K_{\text{HR}}K_2 C_{\text{Ni,aq}}C_{\text{HR,org}}} \quad , \tag{11}$$

where as $k_{\text{T}}$ is the average reaction rate constant of nickel in the vibro-mixer type extractor.

When $C_{\text{HR,org,0}}$ is in large excess of $C_{\text{Ni,aq,0}}$, $C_{\text{HR,org}}$ can be approximated as $C_{\text{HR,org,0}}$. Further, when the ammonium sulfate concentration in the aqueous solution is in large excess of the $C_{\text{Ni,aq,0}}$, the proton concentration released from the extractant by the extraction reaction was considered to be buffered sufficiently by the ammonium sulfate aqueous solution. Hence, $C_{\text{H+,aq}}$ can be approximated as $C_{\text{H+,aq,0}}$. The extractant and the proton concentrations are represented as follows:

$$C_{\text{HR,org}} \qquad C_{\text{HR,org, 0}} \tag{12}$$

$$C_{\text{H+,aq}} \qquad C_{\text{H+,aq,0}} \qquad . $$

$$\text{(13)}$$

Substituting Eqs. (12) and (13) into Eq. (11), the following equation is obtained;

$$\frac{\tau C_{\text{HR,org,0}}}{C_{\text{Ni,aq,0}}E} = \frac{1}{k_{\text{T}}} \times \frac{(1 + K_{\text{HR}}C_{\text{HR,org,0}})C_{\text{H+,aq,0}}}{K_{\text{HR}}K_2 C_{\text{HR,org,0}}} \quad \frac{1}{C_{\text{Ni,aq}}} + \frac{1}{k_{\text{T}}} \quad . \tag{14}$$

The experimental values of $\tau C_{HR,org,0}/(C_{Ni,aq,0}E)$ for various $C_{H+,aq,0}$ and $C_{HR,org,0}$ were plotted against the value of $\{(1+K_{HR}C_{HR,org,0})C_{H+,aq,0}/(K_{HR}K_2C_{HR,org,0})\}(1/C_{Ni,aq})$, as shown in **Fig. 8**. Except for the experimental results at 800 spm, all experimental results are scattered along straight lines, which have different slopes for the respective vibration frequencies. From the slopes of the straight lines in Fig. 8, the values of the average reaction rate constant, $k_T$, at a frequency lower than 500 spm were determined as shown in **Table 1**. The solid lines in Figs. 3, 4, 5, 6 and 7 are the calculated results by the Newton-Raphson method using Eq. (11) with the values of $k_T$ for each frequency in Table 1. At a frequency lower than 500 spm, the calculated results agreed with the behavior of the experimental results. The average reaction rate constant at 800 spm could not determine due to large scatter of the data in Fig. 8. The average reaction rate of nickel in the vibro-mixer type extractor at a frequency lower than 500spm can be interpreted by the interfacial reaction process derived from the Lewis-type transfer cell.

The values of $k_T$ in Table 1 and the value of $k_0$ was compared using the relation, $k_T = 2k_0S/V$, where as $k_0$ is the interfacial reaction rate constant that is 9.5 x $10^{-6}$ dm/sec, $S$ is the interfacial area in the transfer cell that is 1.11 x $10\,cm^2$, and $V$ is the net volume in the vibro-mixer type extractor, 2.27 x $10^{-2}$ $dm^3$. The values of $\log k_T$ in the vibro-mixer type extractor and $k_0$ in Lewis-type transfer cell were plotted in **Fig. 9.** The calculated value of $\log (2k_0S/V)$ in the Lewis-type transfer cell was indicated by a open circle key in Fig. 9. The values of $k_T$ increased with increasing the frequency of the plates. The values of $k_T$ in the vibro-mixer type extractor were enhanced $10^2$-$10^3$ times those of the $2k_0S/V$ obtained in the Lewis-type transfer cell. These large increasing in the reaction rate constants is considered to be an increasing in the interfacial area and in the surface renewal rate due to the formation of small droplets caused by the vibration of the plates in the extractor.

**4. Conclusion**

The extraction rate of nickel in aqueous ammonium sulfate solution with 5-dodecylsalicylaldoxime in kerosene was investigated using a vibro-mixer type extractor. The experimental results correlated to the complete mixing flow in the vibro-mixer type extractor were analyzed based on the interfacial reaction rate. The average reaction rate of nickel with LIX860-IC in a vibro-mixer type extractor was represented by the following equation:

$$r_{Ni} = \frac{C_{Ni,aq,0}E}{\tau} = k_{T} \frac{K_{HR}K_2 C_{HR,org}^2 C_{Ni,aq}}{C_{H+,aq} + K_{HR}C_{HR,aq}C_{H+,aq} + K_{HR}K_2 C_{Ni,aq}C_{HR,org}} .$$

The average extraction rate constants in the vibro-mixer type extractor were $10^2$ to $10^3$ folds larger than that in the Lewis-type transfer cell. This is considered to be due to increase the interfacial area and the surface renewal rate caused the formations of small droplets by high speed mixing of the vibro-mixer type extractor.

### Nomenclature

$C$      concentration (mol/dm$^3$)

$E$      fractional extraction of nickel (–)

$K$      equilibrium constant for the reaction (–)

$K_{HR}$      adsorption equilibrium constant of extractant (dm$^3$/mol)

$K_2$      equilibrium constant of Eq.(4) (–)

$S$      interfacial area in the transfer cell (cm$^2$)

$V$      net volume of the vibro-mixer type extractor (dm$^3$)

$k_0$      interfacial reaction rate constant (dm/sec)

$k_T$      overall reaction rate constant observed in the vibro-mixer type extractor (sec$^{-1}$)

$r$      reaction rate in the Lewis-type transfer cell (mol/(dm$^2$sec))

$r'$      average reaction rate using the vibro-mixer type extractor (mol/(dm$^3$sec))

θ        fraction of active site at interface (–)

τ        mean residence time of fluids in the extractor (sec)

**Subscripts**

org      organic solution

aq       aqueous solution

HR       5-dodecylsalicylaldoxime

Ni       nickel

0        initial

## References

[1]    C. S. Brooks, *Sep. Sci. Technol.* **28** (1993) 579.

[2]    M. Niinae, A. Itoh, K. Kenchu, *Shigen to Sozai* **114** (1998) 63 (in Japanese).

[3]    M. Tanaka M. Kobayashi, M. A. S. Alghamdi, K. Tatsumi, *Shigen to Sozai* **117** (2001) 507 (in Japanese).

[4]    T. Sana, K. Shiomori, Y. Kawano, K. Nagayoshi, *Solv. Extr. Res. Devel., Jpn.* **7** (2000) 206.

[5]    T. Sana, K. Shiomori, Y. Kawano, K. Nagayoshi, *ARS Separatoria Acta* **1** (2002) 35.

[6]    T. Sana, K. Nagayoshi, K. Shiomori, Y. Baba, Y. Kawano, *Kagaku Kogaku Ronbunshu* **23** (1997) 243 (in Japanese).

[7]    T. Sana, K. Shiomori, Y. Kawano, *ARS Separatoria Acta* **2** (2004) 125.

[8]    Y. Kawano, S. Kiyoyama, K. Shiomori, Y. Baba, T. Hano, *J. Ferment. Bioeng*. **78** (1994) 293.

[9]    Y. Kawano, K. Shiomori, S. Osada, S. Yamada, Y. Baba, H. Yoshizawa, Y. Hatate, *Solv. Extr. Res. Devel., Jpn*. **6** (1999) 51.

[10]   K. Yoshizuka, H. Arita, Y. Baba, K. Inoue, *Hydrometallurgy* **23** (1990) 247.

**Figure captions**

Fig. 1  Schematic diagram of a vibro-mixer type extractor

Fig. 2  The experimental apparatus

Fig. 3  Effect of the frequency of the vibration plates on $C_{\text{Ni,org}}$, for various $C_{\text{Ni,aq,0}}$ at $\tau =$ 20 sec.

Fig. 4  Effect of the frequency of the vibration plates on $C_{\text{Ni,org}}$, for various $C_{\text{Ni,aq,0}}$ at $\tau =$ 30 sec.

Fig. 5  Effect of the frequency of the vibration plates on $C_{\text{Ni,org}}$ for various $C_{\text{HR,org,0}}$.

Fig. 6  Effect of the frequency of the vibration plates on $C_{\text{Ni,org}}$ for various pH values.
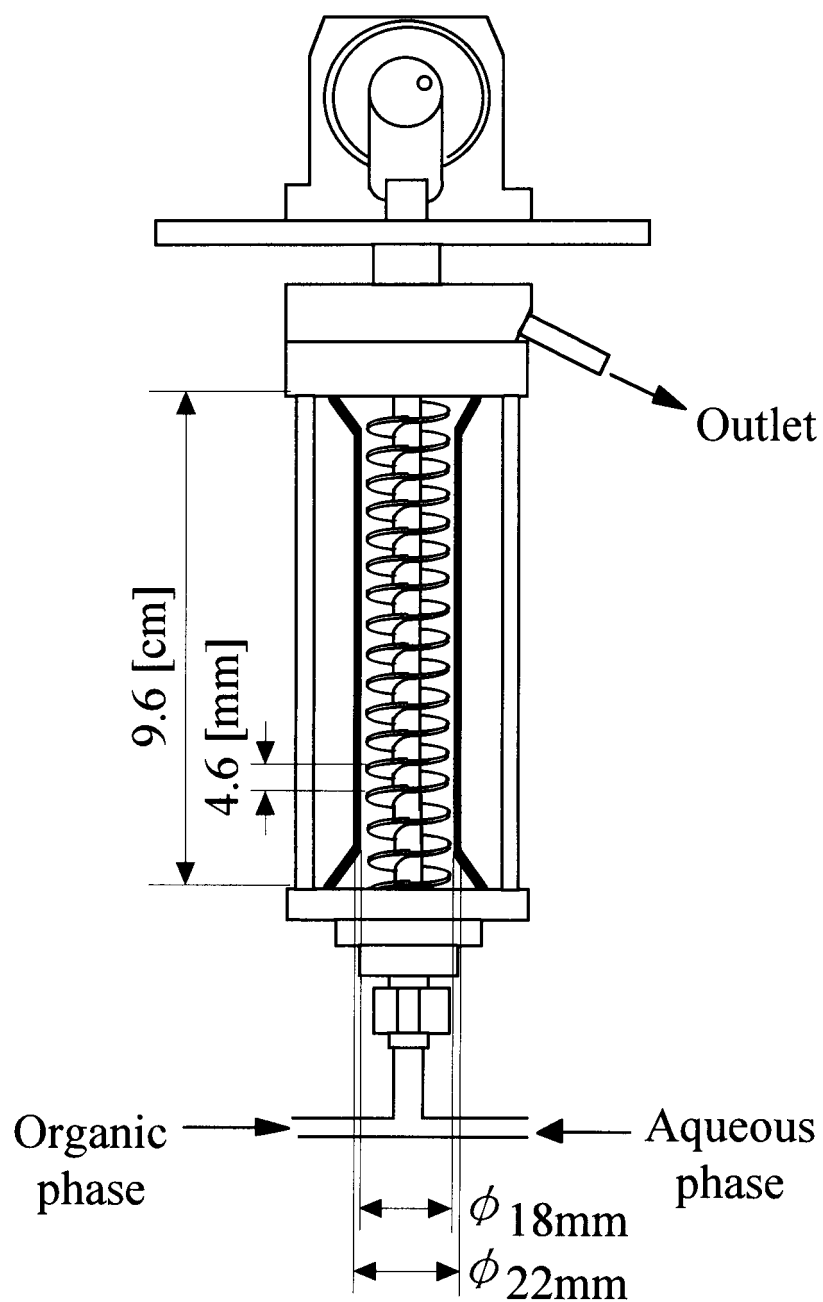
Fig. 7  Effect of the frequency of the vibration plates on $C_{\text{Ni,org}}$ for various average residence time in the extractor.

Fig. 8  Relationship between  $C_{\text{HR,org,0}}/C_{\text{Ni,aq,0}}E$ and $(1+K_{\text{HR}}C_{\text{HR,org,0}})C_{\text{H+,aq,0}}/(K_{\text{HR}}K_2C_{\text{HR,org,0}})(1/C_{\text{Ni,aq}})$ for various frequency.

Fig. 9  Relationship between the frequency of the vibration plates and the values of $\log k_{\text{T}}$ and $\log(2k_0 S/V)$

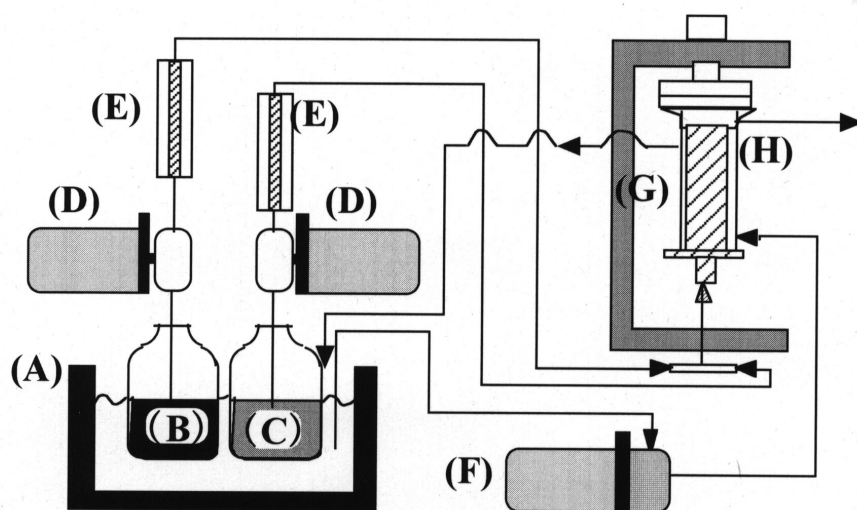Table 1  The average extraction rate constants for each frequency

| Frequency [spm] | $k_T$ [sec$^{-1}$] |
|---|---|
| 100 | $8.7 \times 10^{-3}$ |
| 150 | $1.5 \times 10^{-2}$ |
| 200 | $2.1 \times 10^{-2}$ |
| 250 | $3.5 \times 10^{-2}$ |
| 300 | $6.1 \times 10^{-2}$ |
| 500 | $8.1 \times 10^{-2}$ |

Outlet

9.6 [cm]

4.6 [mm]

Organic phase

Aqueous phase

$\phi$ 18mm

$\phi$ 22mm

Net volume: $2.27 \times 10^{-2}$ [dm³]

Fig. 1

Sana, Shiomori, Kawano

(A) Constant temperature waterbath     (E) Flow meter

(B) Aqueous solution feed tank     (F) Circulating pump

(C) Organic solution feed tank     (G) Constant temperature waterjacket

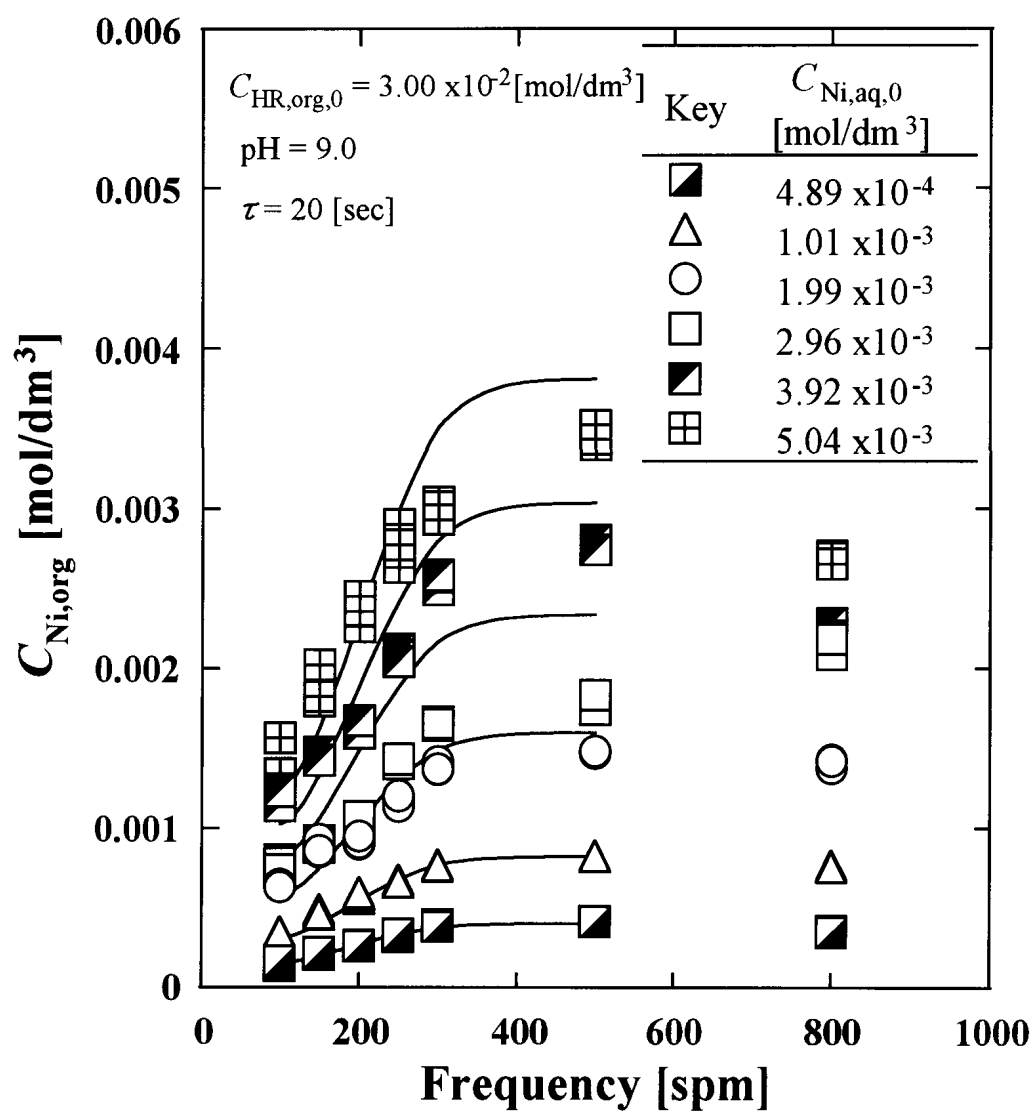(D) Metering pump     (H) Vibro-mixer type extractor

**Fig. 2**

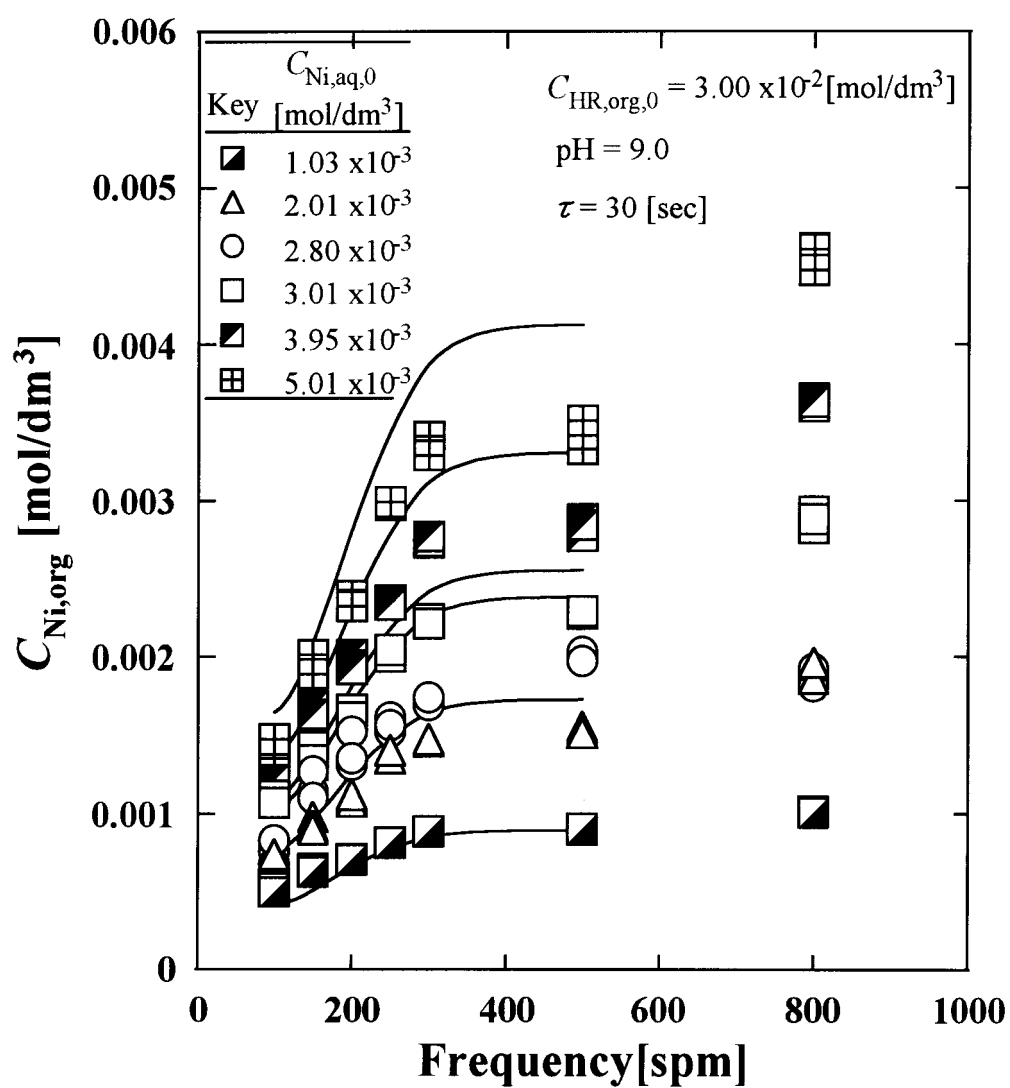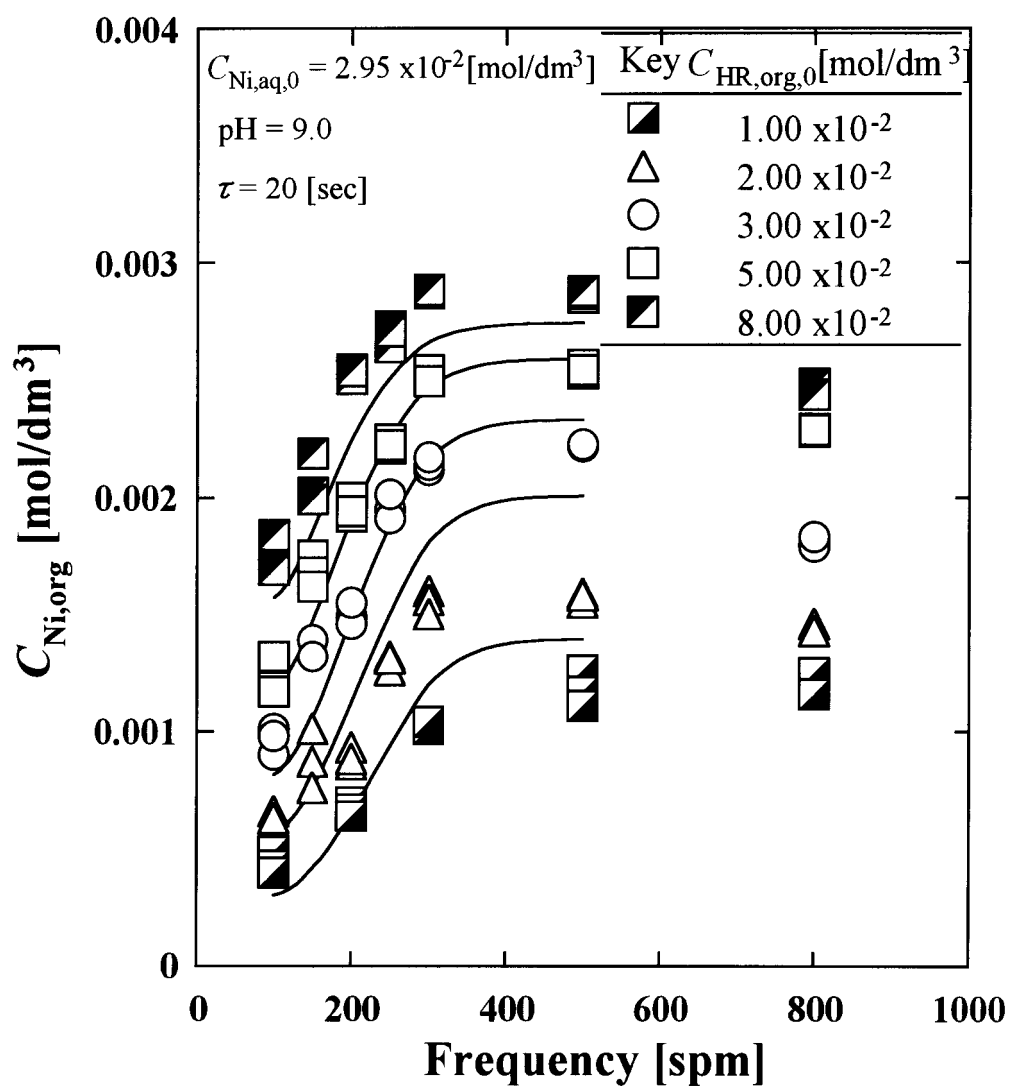Sana, Shiomori, Kawano

$C_{HR,org,0} = 3.00 \times 10^{-2} [\text{mol/dm}^3]$

pH = 9.0

$\tau = 20$ [sec]

| Key | $C_{Ni,aq,0}$ [mol/dm$^3$] |
|---|---|
| ◪ | $4.89 \times 10^{-4}$ |
| △ | $1.01 \times 10^{-3}$ |
| ○ | $1.99 \times 10^{-3}$ |
| □ | $2.96 \times 10^{-3}$ |
| ◪ | $3.92 \times 10^{-3}$ |
| ⊞ | $5.04 \times 10^{-3}$ |

**Fig. 3**

Sana, Shiomori, Kawano

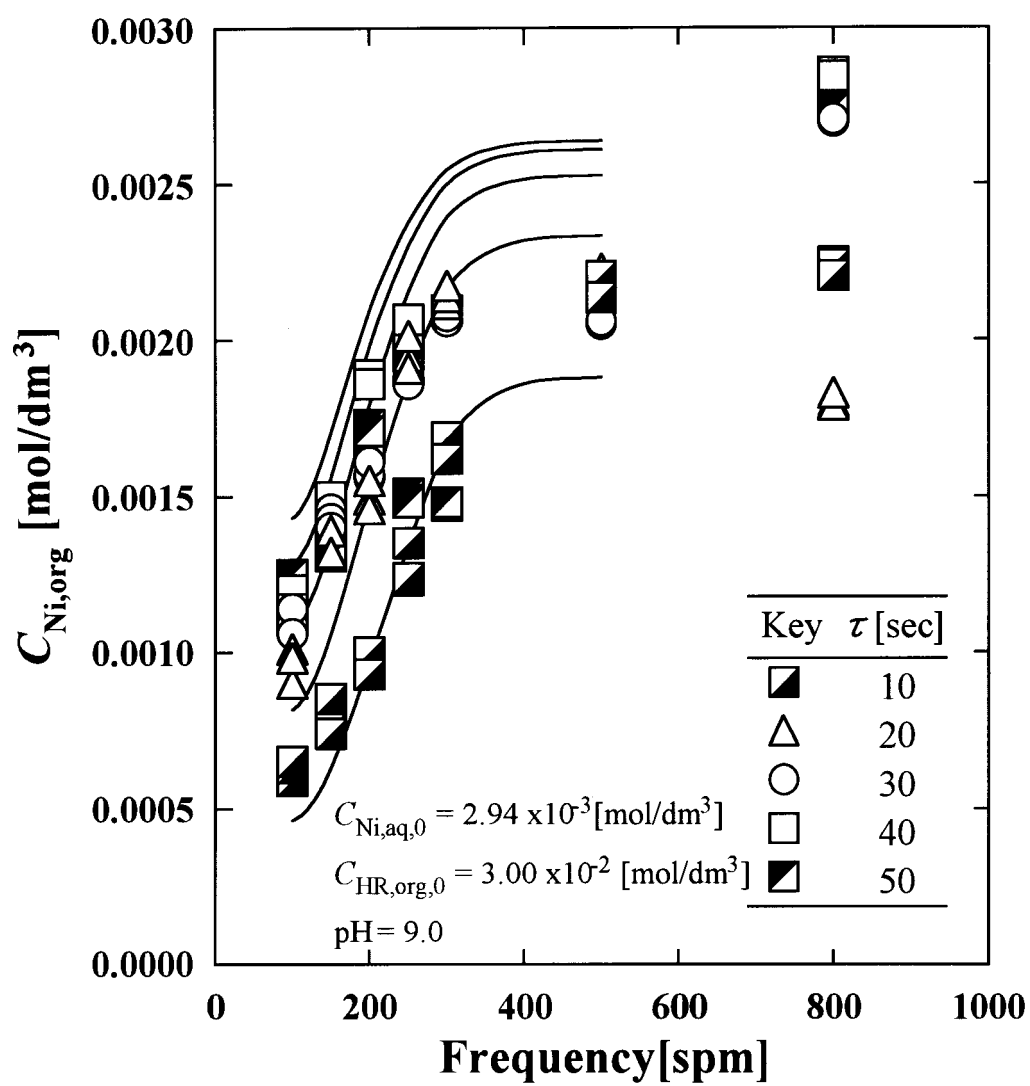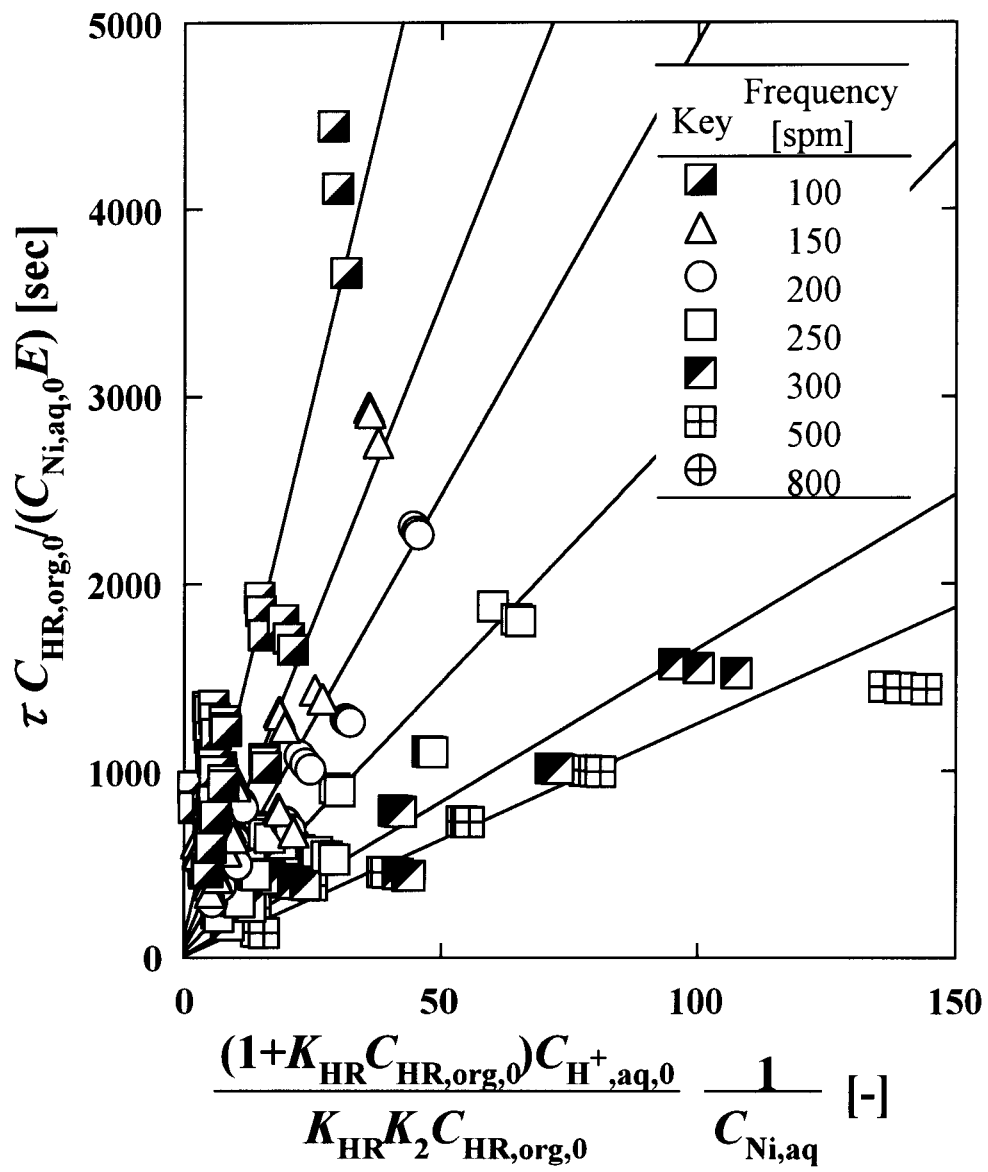**Fig. 4**

Sana, Shiomori, Kawano

Fig. 5

Sana, Shiomori, Kawano

$C_{Ni,aq,0} = 3.00 \times 10^{-3} [mol/dm^3]$

$C_{HR,org,0} = 5.00 \times 10^{-2} [mol/dm^3]$

$\tau = 20 [sec]$

| Key | pH[-] |
|-----|-------|
| ◪ | 7.5 |
| △ | 8.0 |
| ○ | 8.5 |
| □ | 9.0 |
| ◩ | 9.5 |

X-axis: **Frequency [spm]**

Y-axis: $C_{Ni,org} [mol/dm^3]$

**Fig. 6**

Sana, Shiomori, Kawano

**Fig. 7**

Sana, Shiomori, Kawano

**Fig. 8**

Sana, Shiomori, Kawano

**Fig. 9**

Sana, Shiomori, Kawano